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METHOD FOR MANUFACTURING SUBSTRATE WITH FINE PATTERN
[BISAI PATAN TSUKI KIBAN NO SEIZO HOHO]

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Specification

1. Title of the Invention

Method for Manufacturing Substrate with Fine Pattern

2. Claims

1) A method for manufacturing a substrate with a fine pattern, wherein a film on which a solution containing a metallic organic compound is spread is formed on a substrate and/or a mold having a fine pattern; a film with a fine pattern having a concave and convex shape corresponding to a concave and convex shape of the mold is formed on the substrate by pressing said substrate and said mold against each other, and said film is solidified; said method for manufacturing a substrate with a fine pattern being characterized in that the mutual press of said mold and said substrate is started from one optional end and then advanced to the other part.

2) The method for manufacturing a substrate with a fine pattern of Claim 1, characterized in that said substrate and said mold have a disk shape; and said mutual press is an operation that is started from the central part of the disk of said mold and said substrate and axially symmetrically advanced in the outer peripheral direction.

¹ Numbers in the margin indicate pagination in the foreign text.

- 3) The method for manufacturing a substrate with a fine pattern of Claim 1 or 2, characterized in that a tackifier is included in said solution; and said mutual press process is carried out in a pressure-reduced atmosphere.
- 4) The method for manufacturing a substrate with a fine pattern of Claim 3, characterized in that the pressure of said pressure-reduced state is 1,333 Pa (10 Torr) or lower.
- 5) The method for manufacturing a substrate with a fine pattern of any of Claims 1-4, characterized in that said substrate is a glass substrate.
- 6) The method for manufacturing a substrate with a fine pattern of any of Claims 1-5, characterized in that said mutual press is carried out after said mold is deformed into a curved surface.

3. Detailed Description of the Invention

[Industrial Application Field]

The present invention relates to a method for manufacturing a substrate with a fine pattern. In particular, the present invention relates to a method for manufacturing a substrate with a fine pattern suitable for the use in substrates with grooves for optical disks, diffraction gratings, etc.

[Prior Art]

Methods for manufacturing a substrate with grooves that forms a flexible spread film of a solution containing a metallic organic compound on a substrate, transfers a

groove shape corresponding to a peak shape of a mold onto said spread film by pressing the mold and solidifies said spread film by baking. (For example, Japanese Kokai Patent Application Nos. Sho 62[1987]-102445, Sho 62[1987]-225273, and Sho 63[1988]-158168.)

[Problems to Be Solved by the Invention]

According to the method for manufacturing a substrate with grooves, using a substrate and a spread film and a mold prepared on the substrate. Therefore, since a metallic organic compound was installed in a film state on the substrate, the contraction was small, compared with a gel body, and cracks or warps were difficult to be generated. However, large foams frequently remained as defects between the press mold and the substrate with said spreading surface, lowering the yield of the product.

[Means to Solve the Problems]

In order to solve the aforementioned problems, in a method for manufacturing a substrate with a fine pattern, wherein a film on which a solution containing a metallic organic compound is spread is formed on a substrate and/or a mold having a fine pattern, a film with a fine pattern having a concave and convex shape corresponding to a concave and convex shape of the mold is formed on the substrate by pressing said substrate and said mold against each other, and said film is solidified, the mutual

press of said mold and said substrate is started from one optional end and then advanced to the other part.

As said substrate and said mold, any optional shape can be used as long as it is a sheet shape. In case these substrate and mold have a disk shape, their mutual press is preferably started from the central part and axially symmetrically advanced in the outer peripheral direction in terms of axial alignment of said substrate and said mold.

In addition, as the material of said substrate, glasses are preferably used in terms of optical properties, mechanical properties, etc., and among them, glasses containing an alkali metal such as Na and K, which can be chemically reinforced, are especially preferable used.

Moreover, as the material of said mold, metals, glasses, resins, etc., are used. Among them, a mold made of nickel that is prepared by nickel electroforming, a mold made of glass and resin that is prepared by 2P method, a mold made of resin that is prepared by an injection molding method, and a mold made of resin through a casting method are preferably employed in terms of size precision.

Furthermore, said mutual press process is preferably carried out under reduced pressure because the size of defects is reduced, even if foams are confined between said substrate and the substrate with said spread film. In particular, the

pressure in said pressure-reduced state is preferably 1,333 Pa (10 Torr) or lower because the size of generating defects is sufficiently reduced. In addition, in the present invention, a tackifier is included in the aforementioned solution, and the mutual press process is carried out under reduced pressure. However, if the mutual press process is carried out under reduced pressure in a state in which no tackifier is included, the solvent in the spread film is volatilized, and the solidification is rapidly advanced, thus being unable to realize a good mutual press.

The tackifier, which is used in the present invention, has an effect of raising the viscosity of the solution containing the aforementioned metallic organic compound and facilitates the formation of the spread film. At the same time, in case the mutual press process of the substrate and the mold is carried out under reduced pressure, the spread film is maintained in a soft state (appropriate viscous state) for a long time, even under reduced pressure, and patterning is made easy. As said tackifier, polymeric materials soluble in an organic solvent are preferably used. Among them, chain-shaped polyethers such as polyethylene glycol and polytetramethylene ether glycol are preferably used.

In addition, the amount of addition of these polyethylene glycol, polytetramethylene ether glycol, etc., is preferably

about 0.25-1.8 times of the weight of an oxide which is generated by said spreading solution. (If the amount of addition is 0.25 times or less, the spread film is apt to be cured during the decompression, making patterning difficult. On the contrary, if the amount of addition is 1.8 times or more, the spread film is too softened, easily causing mold collapse, etc.)

The aforementioned metallic organic compound is used alone or mixed with water and an organic solvent such as alcohol, the aforementioned tackifier, and if necessary, a hydrolysis catalyst of an acid or alkali as a mixture to form a solution for spreading.

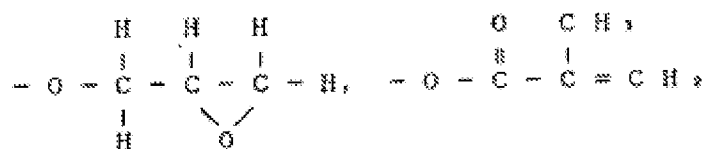
As the fine pattern of the mold, various shapes can be used. For example, a fine pattern with a shape, which has a width of about 1 μm usable as a guide groove for optical disks and has a depth of 50-200 nm, and a pattern with a shape of several 100 nm usable as a diffraction grating or grating lens can be used.

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As the metallic organic compound that is used in the present invention, any compound that raises the viscosity of the solution by causing a polycondensation or crosslinking reaction.

For example, metallic organic compounds containing a general functional group for a polycondensation or crosslinking

reaction, such as metal alcoholate, chelate complex, $-\text{COOH}$, $-\text{COOR}$, $-\text{NH}_2$,



which are used in a method ordinarily called a sol-gel process and represented by $\text{M}(\text{OR})_n$ (M represents a metal such as Si, Ti, Zr, Ca, Al, Na, Pb, B, Sn, and Ge, R represents an alkyl group such as methyl and ethyl, and n represents an integer of 1-4) such as $\text{Si}(\text{OCH}_3)_4$, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, $\text{Al}(\text{OC}_3\text{H}_7)_3$, $\text{Al}(\text{OC}_4\text{H}_9)_3$, and NaOC_2H_5 , can be mentioned. Among them, metal alcoholate is preferably used.

As the method that starts the mutual press of said mold and said substrate from one optional end, for example, a method that uses a mold made of a material with low rigidity such as organic material as said mold, deforms said mold into a convex curved surface such as spherical surface or cylindrical surface shape, contacts said mold and said substrate, and releases said deformation, etc., can be mentioned.

[Operation]

According to the present invention, in the mutual press process of the mold and the substrate, since a gas existing in the gap between the mold and the substrate by the surface

tension of a sol-gel film is expelled from the gap, few foams are generated in the spread film.

[Application Examples]

Application Example 1

0.05 mol silicon tetraethoxide was weighed, and ethanol of 5 times and water of 6 times (containing 3 wt% HCl) as a mole ratio were added to it and stirred at about 50°C for 1 h. This solution was diluted by adding ethanol at an amount of twice, and polyethylene glycol (PEG₆₀₀) with a molecular weight of 600 was added at an amount of $(\text{PEG}_{600})/(\text{SiO}_2) = 1.0$ as a weight ratio to SiO₂ as a final product, uniformly dissolved, and adopted as a spreading solution.

A disk substrate 1 made of chemically reinforced glass with an outer diameter of 130 mm and a thickness of 1.2 mm was immersed into this spreading solution and slowly pulled up to form a spread film 2 on the substrate. Next, as shown in Figure 1, the spread film was sandwiched between a mold 3 made of polycarbonate with an outer diameter of 130 mm and a thickness of 1.2 mm, having peak parts with a spiral shape with a peak height of 0.14 μm, a peak width of 0.7 μm, and a peak interval of 1.6 μm in a range of a radius of 25-60 mm, and this glass substrate, and a silicone rubber plate 4 with an outer diameter of 130 mm and a thickness of 5 mm was installed into the mold oppositely to the substrate. Next, the peripheral part of said

mold 3 was fixed, and the central part was pressed by about 2-3 mm to deform the side opposite to the glass substrate into an appropriate spherical surface shape as a convex shape. In this state, the mold was slowly, mutually pressed against the glass substrate from the disk center part. Next, while loosening the deformation of the mold, the mutual press is carried out, and the mutual press part is axially symmetrically extended in the radial direction. Finally, the entire disk surface was pressed.

Next, heating is applied in this state, and baking is carried out at 100°C for 10 min. At that time, the mold and the glass disk were separated, and the glass disk was further baked at 400°C for 10 min. With this baking operation, the spread film was changed to an amorphous film with a thickness of about 0.2 μm similar to a glass body by the flight and dispersion of ethanol, water, etc.

When the surface of the glass disk with grooves was observed by a polarizing microscope, a good groove shape with a groove depth of about 0.1 μm , a groove width of about 0.7 μm , and a groove interval of about 1.6 μm was obtained on the entire surface, and the mixture of foams was little recognized.

Application Example 2

0.05 mol silicon tetraethoxide was weighed, and ethanol of 4 times and water of 4 times (containing 3 wt% HCl) as a mole ratio were added to it and stirred at about 50°C for 30 min. A

solution in which 0.01 mol titanium tetra-normal butoxide was diluted with ethanol was slowly added to said solution and stirred at about 50°C for 30 min. This solution was diluted by adding ethanol at an amount of twice, and polyethylene glycol (PEG₆₀₀) with a molecular

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weight of 600 was added at an amount of $(\text{PEG}_{600})/(\text{SiO}_2 + \text{TiO}_2) = 1.0$ as a weight ratio to $\text{SiO}_2 + \text{TiO}_2$ as final products, uniformly dissolved, and adopted as a spreading solution.

Through an operation similar to that of Application Example 1 except using the aforementioned spreading solution, a glass disk with grooves was prepared.

When the surface of the glass disk with grooves prepared in this application example was observed by a polarizing microscope, a good groove shape with a groove depth of about 0.1 μm , a groove width of about 0.7 μm , and a groove interval of about 1.6 μm was obtained on the entire surface, and the mixture of foams was little recognized.

Application Example 3

A disk substrate 5 made of chemically reinforced glass with a length of 100 mm, a width of 150 mm, and a thickness of 1 mm was immersed into this spreading solution prepared in Application Example 1 and slowly pulled up to form a spread film 2 on the substrate. Next, as shown in Figure 2, the spread film

2 was sandwiched between a mold 6 made of polycarbonate with a length of 100 mm, a width of 150 mm, and a thickness of 1.2 mm, having peak parts with a peak height of 0.5 μm , a peak width of 0.7 μm , and a peak interval of 1.6 μm , and this glass substrate, and a silicone rubber plate 4 with a length of 100 mm, a width of 150 mm, and a thickness of 5 mm was installed into the mold oppositely to the substrate. Next, said mold was wound on a cylindrical undercoat material, and the side opposite to the glass substrate was deformed into a cylindrical surface shape as a convex shape. In this state, the mold was slowly, mutually pressed against the glass substrate from the end. Next, while releasing the mold 6 of the mutual press part from the cylindrical undercoat material, the mutual press is carried out, and the mutual press part is unidirectionally extended. Finally, the entire surface was pressed.

Next, heating is applied in this state, and baking is carried out at 100°C for 10 min. At that time, the mold and the glass substrate were separated, and the glass substrate was further baked at 400°C for 10 min. With this baking operation, the spread film was changed to an amorphous film with a thickness of about 0.2 μm similar to a glass body by the flight and dispersion of ethanol, water, etc.

When the surface of the glass substrate with grooves was observed by a polarizing microscope, a good groove shape with a

groove depth of about 0.36 μm , a groove width of about 0.7 μm , and a groove interval of about 1.6 μm was obtained on the entire surface, and the mixture of foams was little recognized.

Comparative Example

As shown in Figure 3, using materials and a method similar to those of Application Example 1 except for slowly, mutually pressing the entire disk surface against the glass substrate in a flat state in which the mold was not mutually pressed while bending, a glass disk with grooves was prepared.

When the surface of the glass disk with grooves prepared by this operation was observed by a polarizing microscope, a good groove shape with a groove depth of about 0.1 μm , a groove width of about 0.7 μm , and a groove interval of about 1.6 μm was partially obtained, however the mixture of foams into many parts was recognized.

[Effect of the Invention]

According to the present invention, a fine pattern can be uniformly formed with high precision on a large area without generating defects.

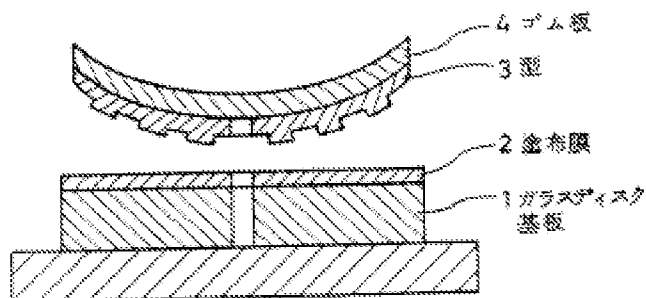
4. Brief Description of the figures

Figure 1 is a cross section showing the outline of the mutual press method of the present invention described in Application Example 1, Figure 2 is a cross section showing the outline of the mutual press method of the present invention

described in Application Example 3, and Figure 3 is a cross section showing the outline of a mutual press method of a comparative example.

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Figure 1



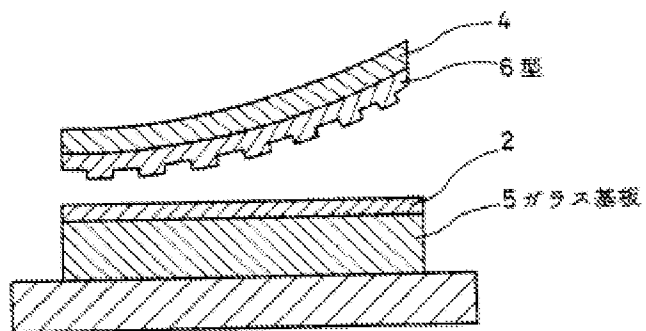
1: Glass Disk Substrate

2: Spread Film

3: Mold

4: Rubber Plate

Figure 2



5: Glass Substrate

6: Mold

Figure 3

